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The Aqueous Complexation of Morin and its Sulfonate Derivative with Lanthanum(III) and Trivalent Lanthanide

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Corresponding Author:	Maxim Alexandrovich Lutoshkin, Ph.D. Institute of Chemistry and Chemical Technoloology of the Siberian Branch of the RAS Krasnoyarsk, RUSSIAN FEDERATION
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Institute of Chemistry and Chemical Technoloology of the Siberian Branch of the RAS
Corresponding Author's Secondary Institution:	
First Author:	Maxim Alexandrovich Lutoshkin, Ph.D.
First Author Secondary Information:	
Order of Authors:	Maxim Alexandrovich Lutoshkin, Ph.D.
	Alexander I. Petrov
	Boris N. Kuznetsov
	Alexandr S. Kazachenko
Order of Authors Secondary Information:	
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Abstract:	The complexation of flavonoids Morin and morin-5'-sulfonic acid (MSA) with rare earth metals is studied in aqueous solution using absorption spectroscopy. In this research 50 conditional and 26 “true” equilibrium stability constants of monocomplex species were determined for various values of pH at constant ionic strength I=1 ($NaClO_4$). The interactions are investigated for La^{3+} and 12 lanthanides (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+}, Tm^{3+}, Yb 3+, Lu^{3+}). The obtained “true” stability constants (K) lie within 6.7-8.0 logarithmic units. The increase of logK is observed in the order: La≈Pr<Nd≈Ce<Sm≈Eu≈Tb<Gd≈Dy<Er<Tm<Yb≈Lu and Pr≈Nd≈Ce<Gd≈La <Tb<Sm≈Eu<Dy<Er<Tm<Yb≈Lu for morin and MSA, respectively. The DFT calculations with three basis sets functions (Def2-SVP, Def2-TZVP and Def2-TZVPD) were applied for evaluation of theoretical logK and comparative analysis of La(III)-flavonoids interactions.
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The Aqueous Complexation of Morin and its Sulfonate Derivative with Lanthanum(III) and Trivalent Lanthanide

Maxim A. Lutoshkin[a,b§], Alexander I. Petrov[b], Boris N. Kuznetsov[b,c] and Alexandr S. Kazachenko[b]

[a]Université de Lyon, Université Claude Bernard Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, France

[b]Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS", Krasnoyarsk, Russian Federation

[c]Institute of Non-Ferrous Metals and Materials Science, Siberian Federal University, Krasnoyarsk, Russian Federation

[§]**Corresponding author**. E-mail: maximsfu@yahoo.com

The complexation of flavonoids Morin and morin-5'-sulfonic acid (MSA) with rare earth metals is studied in aqueous solution using absorption spectroscopy. In this research 50 conditional and 26 "true" equilibrium stability constants of monocomplex species were determined for various values of pH at constant ionic strength I=1 ($NaClO_4$). The interactions are investigated for La^{3+} and 12 lanthanides (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}). The obtained "true" stability constants (K) lie within 6.7-8.0 logarithmic units. The increase of logK is observed in the order: La≈Pr<Nd≈Ce<Sm≈Eu≈Tb<Gd≈Dy<Er<Tm<Yb≈Lu and Pr≈Nd≈Ce<Gd≈La <Tb<Sm≈Eu<Dy<Er<Tm<Yb≈Lu for morin and MSA, respectively. The DFT calculations with three basis sets functions (Def2-SVP, Def2-TZVP and Def2-TZVPD) were applied for evaluation of theoretical logK and comparative analysis of La(III)-flavonoids interactions.

Keywords: Morin; Flavanoids; Lanthanides complexation; O-donor ligands

1 Introduction

Morin, as naturally occurring flavonoid shows broad spectrum of biological properties: antioxidant [1,2], anticancer [3,4], antibacterial [5], antihypertensive [6] and anti-fibrotic [7] activities. The current flavonol takes part in plant metabolism [8], exhibit inhibitor features toward the α-glucosidase[9] and might be used for protective of cells from ultraviolet [10,11]. In mixture with other flavonoids morin can be isolated from fruits, vegetables and as individual compound from the *Moraceae* family [12]. The numerous solid complexes of morin (and its derivatives) with transition, f- and noble metals are described in literature [13-18]. Some of them, such as complexes with lanthanides [19], copper [20] and chrome [21] displays the biological qualities. The complex formation processes in water media for morin are known only for small numbers of metals [22,23].

As we can see, the various data for solid-state coordination compounds of flavonoids are reported but only few articles are covering problems of complexation processes in liquid. In the same time, especially in solution morin and its complexes have the biological and medicine importance. Therefore, the study of processes between flavonoids and rare earth elements is actually problem. Also, this research is the continue of our previous work [24]. The goal of this research was to investigated of thermodynamic equilibrium characteristics of Morin/MSA-Ln(III) monocomplexes in aqueous solution.

2 Experimental Section

2.1 Apparatus and Procedure

The UV-Vis spectra were measured with the Leki SS2109-UV scanning spectrophotometer (Leki Instruments, Finland) using 1 cm quartz cells. Cell thermostating (±0.1 K) was performed with the Haake K15 thermostat connected to the Haake DC10 controller. The absorbance of process solutions was measured within 220-500 nm. All measurements were performed at 298 K.

2.2 Chemicals Used

All chemicals were of analytical grade: Morin (Sigma-Aldrich), glycine, HCl, H_2SO_4, NaOH, NaCl, $NaClO_4$, $LnCl_3 \cdot 6H_2O$, Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu. All lanthanide chlorides stock solutions were obtained by dissolving in distilled water. The metal salts and ligands were dissolved in distilled water. The morin was dilute in selected sample from water-ethanol solution (50:50 vol.). The concentration of ethanol did not exceed 2% in the final solution. Buffer solutions within the pH range from 2.00 to 3.60 were prepared with glycine and HCl. The accurate desired pH values were obtained by adjusting the molarities of the buffer components in suitable amounts.

2.3 Uv-Vis Measurements

Conditional stability constants (K') for monocomplex species were calculated from the equations (1)-(2) [25]:

$$A^{\lambda}_{calc} = \varepsilon^{\lambda}_{L}(C_L - [ML]) + \varepsilon^{\lambda}_{M}(C_M - [ML]) + \varepsilon^{\lambda}_{ML}[ML], \quad (1)$$

$$[ML] = \tfrac{1}{2}\left[\left(\tfrac{1}{K'} + C_L + C_M\right) + \sqrt{\left(\tfrac{1}{K'} + C_L + C_M\right) - 4C_M C_L}\right], \quad (2)$$

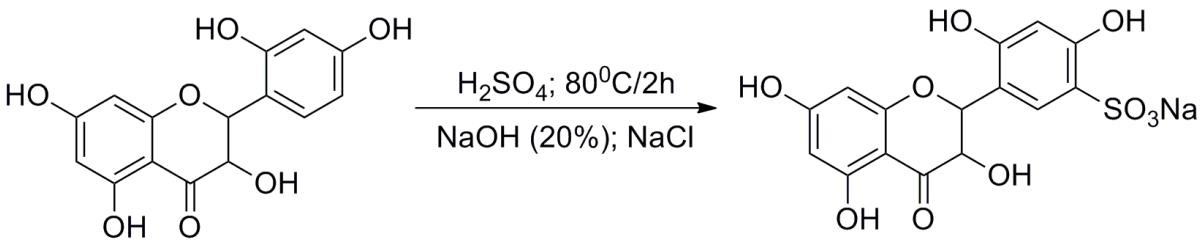
where A^{λ}_{calc} is an absorbance at a given wavelength and C_M and C_L were analytical concentrations of Ln(III) and ligand, respectively. The ε^{λ} is a value of molar extinction coefficient at single wavelength. The optimal values for K' and ε^{λ} were found from the least squares analysis [26]:

$$f(C_M, C_L, K, \varepsilon_i) = \sum_{i=1}^{n} (A_i^{\lambda} - A_i^{calc})^2 \xrightarrow{K,\varepsilon_i} \min . \quad (3)$$

Calculations of all equilibrium constants and molar extinction coefficients were performed using *Wolfram Mathematica* software package [27].

2.5 The synthesis of MSA

The sodium salt of morin-5-sulfonic acid was synthesis by simple method [28]: 2g of pure morin was heated in concentrated sulfuric acid, after this pH of mixture was adjusted to 3-4 with 20% NaOH, and then saturated aqueous NaCl was added (Scheme 1). The obtained crystals were washed with ethanol and tested for quality by paper chromatography. The initial morin is not found in the final product.



Scheme 1. Synthesis of NaMSA.

The reaction form of dihydrate sodium morin-5'-sulfonate in solution is acidic from – morin-5'sulfonic acid[28].

2.5 Ab initio study

The quantum-chemical computations were performed using the GAMESS US [29] program package on the cluster MVS-1000 M of the Institute of computational modeling SB RAS. Geometry optimization was performed by density functional theory (DFT) with the functional PBE0 [30] under Grimme's empirical correction [31]. The Def2-SVP, Def2-TZVP and Def2-TZVPD [32] basis set was applied for C, O, H, S and La(III) atoms. The solvent effects were evaluated using the SMD solvation model [33]. The optimized geometries were visualized with the ChemCraft software.

3 Results and discussions

3.1 UV-vis study

The changes in electronic absorption spectra of morin and MSA is observed in presence of Ln^{3+} ions. All measurements were performed at pH region 2.20-3.00, where studied ligands exists in neutral form [28]. The interaction at pH below 2.20 was excessively low and too great at pH above 3.00, for spectrophotometrically investigation. The all systems were examined under an excess amount of metal ions (C_M>>C_L) for to reduce the possibility of the formation of MH_mL_n species. All spectra were stable over time.

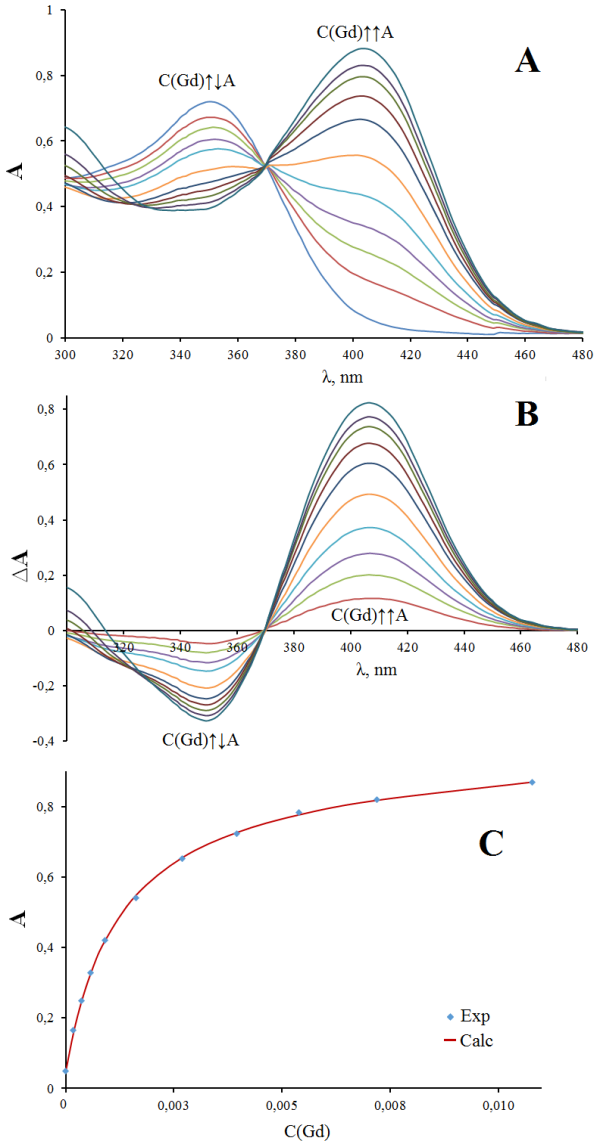


Figure 1. The UV–Vis spectra (A); the ΔA-λ, nm curves (B) and absorbance at single wavelength (C) for Gd(III)-Morin system; C(Morin)= $5.85 \cdot 10^{-5}$ mol·L^{-1}; pH=2.6; I=1

The concentration of ligands was invariant for all series. All spectroscopic data are enclosed in the Supplementary Materials (Table S1-S16). Figure 1 demonstrated the typical transformation in spectra of morin (A); the peak of ΔA^{max} (B) and A^{exp}-A^{calc} for single wavelength (C). The fixed position of ΔA maximum (near 408 nm) at various concentration of Gd^{3+} ions and an excessive concentration of metal indicates about formation only one products (monocomplex species) and the contribution from the poly-nuclear or poly-ligand components is rather negligible. The Job method for this system (Fig. S1) also stated the dominance of ML form. A similar reasoning is applied to every system.

Table 1. Conditional (K'), "true" (K) stability constants and value of extinction for Morin-Ln(III) systems

Ln(III)	pH ± 0.01*	logK' ± 0.03	$\log\varepsilon^{408}$ ± 0.04	logK ± 0.1
La	2.80	2.70	4.13	6.8
Ce	2.20	1.88	4.11	6.7
	2.60	2.41	4.10	6.9
	2.80	2.64	4.15	6.9
	3.00	2.84	4.17	6.9
Pr	2.60	2.42	4.15	6.8
	2.80	2.67	4.16	6.8
	3.00	2.90	4.18	6.9
Nd	2.40	2.31	4.12	6.8
	2.60	2.54	4.13	6.9
	2.80	2.81	4.15	6.9
	3.00	3.03	4.17	7.0
Sm	2.60	2.62	4.16	7.2
Eu		2.66	4.16	7.2
Gd	2.40	2.64	4.18	7.3
	2.60	2.92	4.19	7.4
	2.80	3.17	4.19	7.4
	3.00	3.43	4.20	7.5
Tb	2.20	2.15	4.16	7.2
Dy	2.20	2.20	4.14	7.3
	2.60	2.75	4.18	7.4
	2.80	3.00	4.20	7.5
	3.00	3.25	4.20	7.5
Er	2.80	3.07	4.21	7.6
Tm		3.15	4.20	7.8**
Yb		3.17	4.21	7.9
Lu	2.40	2.70	4.05	7.9

*The "±" values represent confidence limits (P = 0.95) throughout the article.
** Estimate

Thus, all processes occurring in solution can be written as:

$$[Ln(H_2O)_8]^{3+} + H_mL \rightarrow [Ln(H_2O)_{8-k}H_{m-n}L]^{3-n} + kH_2O + nH^+, \quad (4)$$

where L = morin or MSA, glycine and OH^-. For assess the impact of the adverse reactions the following equations [34]:

$$K = \alpha_M \alpha_L K', \quad (5)$$

$$\alpha_M = 1 + \sum \beta_n [L]^n, \quad (6)$$

$$\alpha_L = 1 + \sum K_H [H^+], \quad (7)$$

were used for evaluated of "true" (K) equilibrium stability constants. In equations 5–7 K_H is $1/K_a$ of ligands [35], K' and β_n is the conditional and cumulative stability constants, respectively. The stability constants of glycine-Ln^{3+} [36,37] and hydroxo complexes [38-43] were used for computation of α_M and α_L coefficients (Table S17). The data received are present in Tables 1 and 2.

Table 2. Conditional (K'), "true" (K) stability constants and value of extinction for MSA-Ln(III) systems

Ln(III)	pH ± 0.01	logK' ± 0.04	$\log\varepsilon^{408}$ ± 0.03	logK ± 0.1
La	3.00	3.62	3.79	7.0
Ce	2.80	3.21	3.88	6.9
Pr	2.40	2.81	3.77	6.8
	2.60	3.11	3.77	6.9
	2.80	3.27	3.81	6.9
	3.00	3.54	3.82	7.0
Nd	2.40	2.90	3.90	6.9
	2.60	3.08	3.88	6.8
	2.80	3.32	3.91	6.9
	3.00	3.56	3.92	6.9
Sm	2.80	3.41	3.90	7.2
Eu		3.41	3.89	7.2
Gd		3.34	3.76	7.0
Tb	2.40	2.84	3.75	7.1
Dy	2.80	3.46	3.76	7.4
Er	2.40	3.04	3.75	7.4
	2.60	3.30	3.76	7.5
	2.80	3.53	3.77	7.5
Tm	2.80	3.59	3.77	7.7*
Yb	2.40	3.09	3.76	7.7
	2.60	3.36	3.77	7.8
	2.80	3.59	3.79	7.8
Lu	2.40	3.24	3.73	7.8

* Estimate

The data for stability constant of Tm(III)-glycine complex does not exist in the literature. However, it would be logical to assume that logK for this system is 3.8, because all of other similar values for heavy lanthanides is 3.7-3.9 (Table S18).

It is seen that the obtained logarithmic values of conditional and "true" stability constants lie within 1.8-3.5 and 6.8-7.9, respectively. The analysis of logK'-pH relationship confirmed that only one proton was removed during complexation process (n=1 in eq. 4). Figure 2(A) demonstrated the logK-Ln(III) curves for morin, MSA, quercetin and quercetin-5-sulfonic acid(QSA) [24]. Looking at these curves, one can easily see that morin provide stronger linkages with Ln^{3+} than quercetin. In addition, we can notice that the variance between logK of quercetin and its sulfonate derivative is about 1-2 log units. Quite another picture is present for morin: there is no significant difference between stability of complexes with pure ligand and MSA.

The distribution of points in the Z/R-logK coordinate plane (Figure 2(B)) attests to separate all metals by two groups: La-Gd and Tb-Lu. For both categories of lanthanides the clear correlation between ionic potential and logK is not observe.

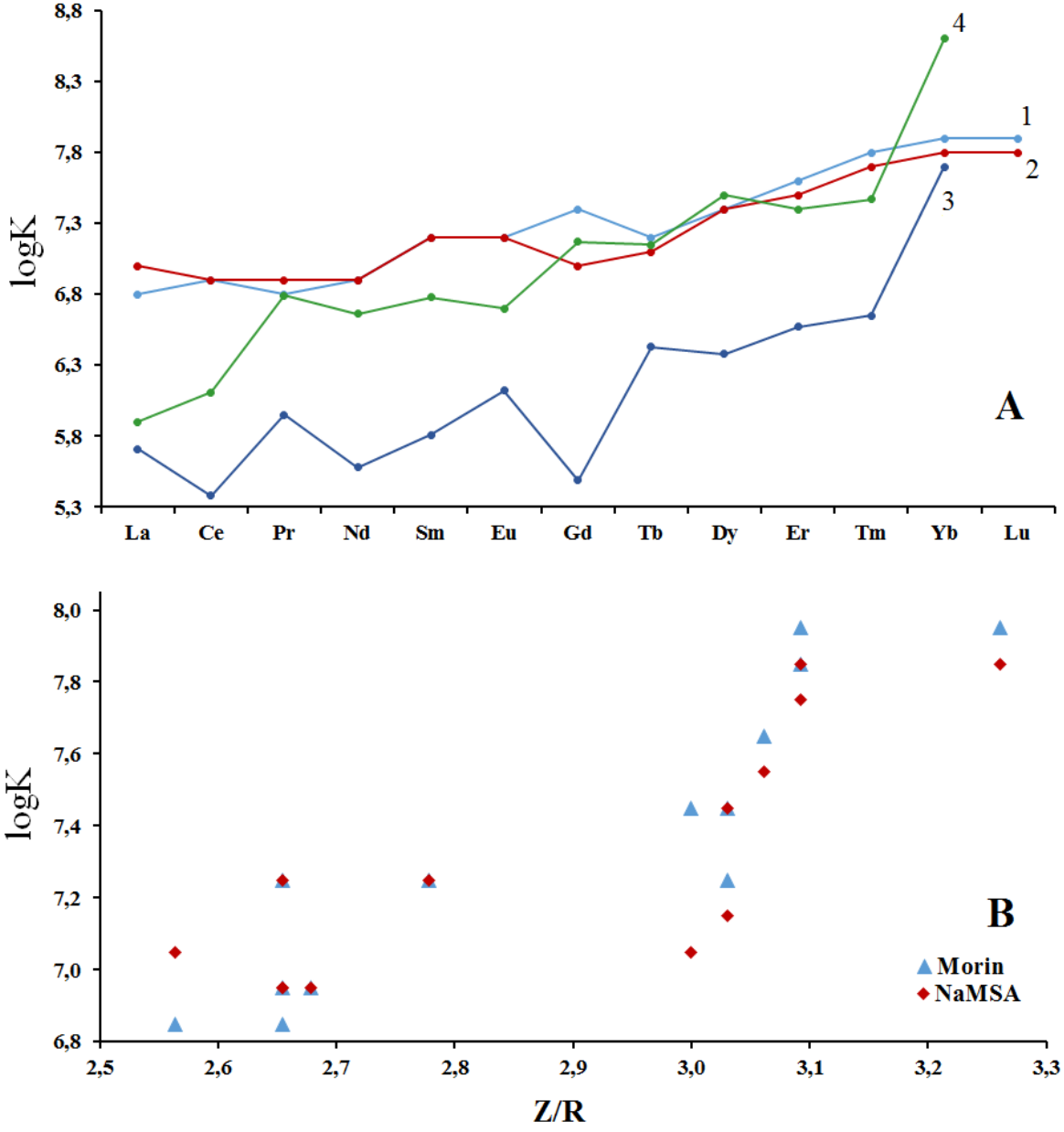


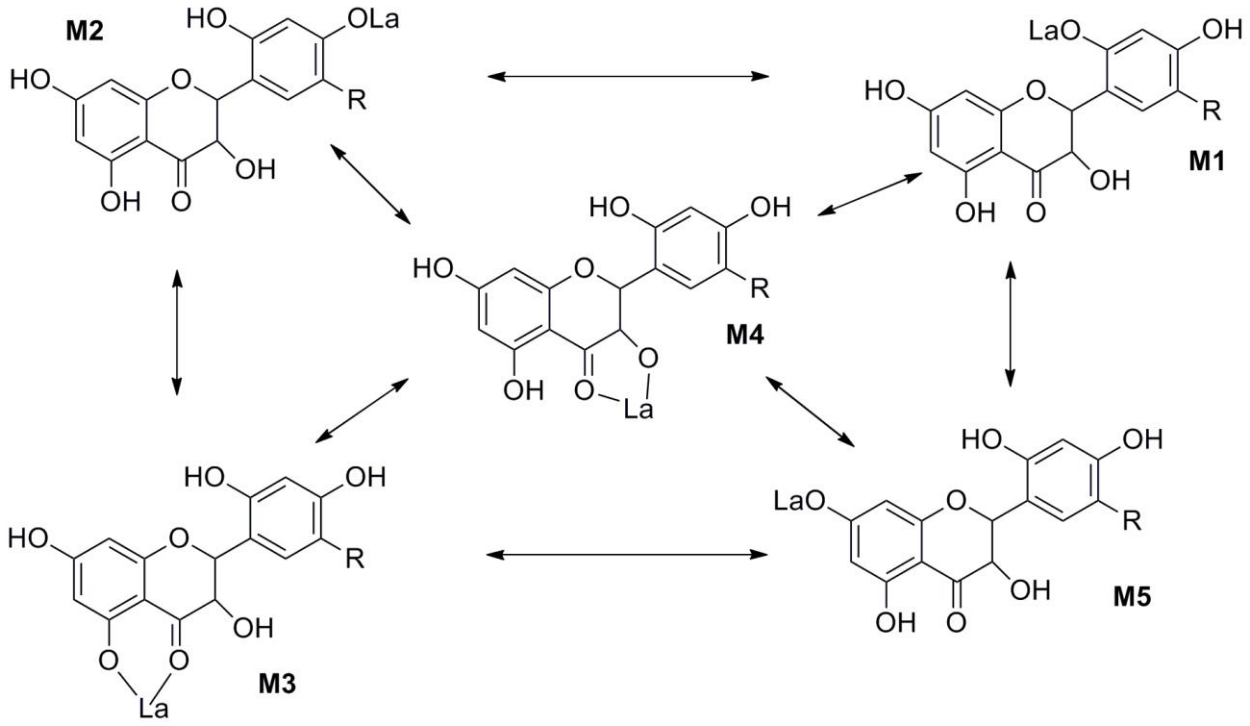
Figure 2. The logK-Ln(III) curves (A) for morin (1), MSA (2), quercetin (3) and quercetin-5-sulfonic acid (4) and logK-Z/R points (B)

Nevertheless, we may conclude that electrostatic contribution more pronounced for Tb-Lu because the points of this group have the trend of increasing logK with increase of Z/R.

3.2. Quantum-chemical calculations

Nowadays, existing quantum-chemical programs do not allow to carry out the effective calculations with such complicated compounds as Ln^{3+}-flavonoids. The modern basis sets functions is not provide SCF-convergence for π-systems with heavy f-elements. Therefore, in this work the predictions of complexes structure and the compare with other flavonoids have been performed only for La^{3+}-complexes. Nevertheless, all results can be extrapolated for all lanthanides due to the isostructural analogy is present for coordination chemistry f-metals in solution [44,45].

The three chelating sites can be produced upon interaction metal ions with flavonoids [22]. Additionally, the non-chelating structures should be taken into account. For the estimate of the stability of each models, the absolute and relativity energies have been found. Since the most common coordination number for lanthanides is equal to eight [46] and morin exhibit the bidentate properties with Ln(III) [47], for DFT calculation k (from eq. 4) was equated 2. The structures of possible isomers are collected at Scheme 2 and calculated energies are given at table 3. In case of MSA the M2 tautomer has two conformations: chelate with O-atom of HSO_3-group and linear structure.



Scheme 2. The Scheme of La(III)-morin (R=H) and La(III)-MSA(R=HSO_3) tautomerism

The minimal energy is observe for tautomers with 3-hydroxyl and 4-carbonyl (structure M4 tautomer) coordination positions, like in case La(III)-quercetin complex [24]. This model is consist with coordination structures proposed for solid morin-lanthanides complexes [47,14]. The visualized theoretical geometry for the most stable isomers of lanthanum(III) complexes with morin and morin-5'-sulfonic acid are illustrated on the Figure 3.

Table 3. The calculated absolute (a.u.) and relative (kJ·mol^{-1}) energies for La(III)-morin/MSA tautomers

tautomer	Morin (R=H)		Morinsulfanate (R=HSO_3)	
	Absolute energy	Relative energy	Absolute energy	Relative energy
M1	-1590.999137	53.6	-2214.180241	30.8
M2	-1590.989970	77.7	-2214.183390	22.5
			-2214.177208	38.7
M3	-1591.013401	16.2	-2214.180289	30.6
M4	-1591.019556	0	-2214.191964	0
M5	-1590.995547	63.0	-2214.159801	84.4

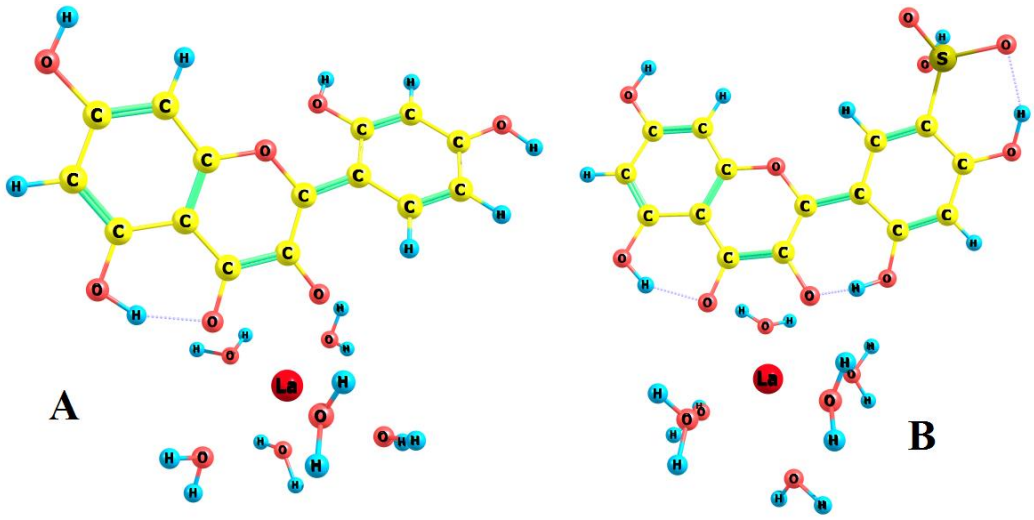


Figure 3. The optimization geometry of La(III)-Morin (A) and La(III)-MSA (B).

For estimate of the influence of different contributions and the compare with other ligands the theoretical value of stability constants La(III)-L (L=morin, quercetin, MSA, QSA) interaction were calculated. The three basis sets (Def2-SVP, -TZVP, -TZVPD) were involve in computationals prodedures from thermodinamic cycle (Figure 4).

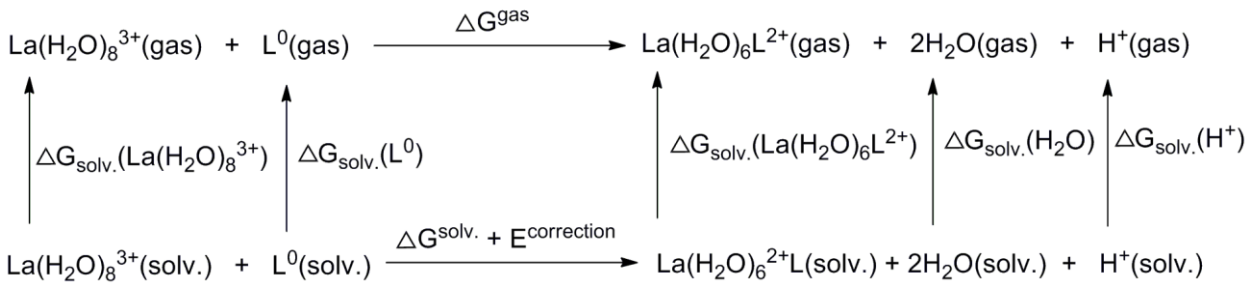


Figure 4. The thermodynamic cycle for calculation of $\log K^{calc.}$

The equilibrium constants were calculated using equations 8-9 [48]:

$$pK_H = \Delta\Delta G^{solv.}/(2.303RT), \quad (8)$$

$$\Delta\Delta G^{solv.} = \Delta G^{gas} + \Delta G^{aq}_{.} + \Delta E^{zpe}, \quad (9)$$

where $\Delta G^{gas/solv}$ and ΔE^{zpe} is the difference between the sum of energy (and zero point levels) of initial and final products, including the correction associated with moving a solvent from a standard-state solution phase concentration of 1 mol·L^{-1} to a standard state of the pure liquid[49]. Table 4 demostrated the theoretical results and contribution of solvation energy in reaction.

Table 4. The theoretical calculated constants and ΔG of solvation

Ligand	$logK^{exp}$	$logK^{calc}$			$-\Delta G^{solv}$, kJ·mol^{-1}		
		Def2-SVP	Def2-TZVPD	Def2-TZVP	Def2-SVP	Def2-TZVPD	Def2-TZVP
Morin	6.80	2.09	11.88	10.55	287.53	253.39	262.40
Quercetin	5.77	1.01	8.64	7.37	262.78	253.28	253.39
MSA	7.00	4.61	10.79	9.45	283.78	273.86	282.93
QSA	5.90	3.40	9.57	8.31	239.75	230.32	240.05

It will be seen from obtained data that Def2-TZVP provide the better approximation for $logK^{calc.}$. The experimatnal order of stability observed for La(III) (MSA>Morin>QSA>Quercetin) is reproduces for Def2-TZVPD and Def2-TZVP basis sets. In considering the value of $\Delta G^{solv.}$ can explain why Morin-Ln(III) complexes is more stable than Quercetin-Ln(III): all theoretical models gives the solvation energy is less for Morin-La(III) system. Analogical reasoning is applied for La(III)-MSA/QSA systems. However, the general order of $logK^{exp}$ is inconsistent with order of $\Delta G^{solv.}$. The presented results demonstrated that studied systems can't be described based only on the electrostatic models. Also, the covalent interaction, specific and non-specific solvation makes a significant contribution to the flavonoid-Ln^{3+} complexation processes.

4. Conclusion

The complexation process of morin and MSA with lanthanides(III) has been studied in aqueous solution. The formation and the domination of 1:1 complexes was shown. The equilibrium stability constants lie between 6.7 and 7.9 logarithmic units. The obtained values are characterize morin and MSA as more effective complexation agent for Ln^{3+} than quercetin.

Through the quantum-chemical calculation at level Def2-SVP/DFT/PBE0/SMD the similarity of complexes structure for morin-Ln(III) and quercetin-Ln(III) has been proposed. The theoretical values of logK were developed with using of functions from Def2 basis set family. The best approach was reached for Def2-TZVP: the discrepancy with $logK^{exp}$ is 1.5-3.5 log units and the convergence with experimental series of ligands-La complex stability take places. The presented computational protocols could be employed for estimate of the order of stability constant of flavonoids-Ln complexation.

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Figure 1

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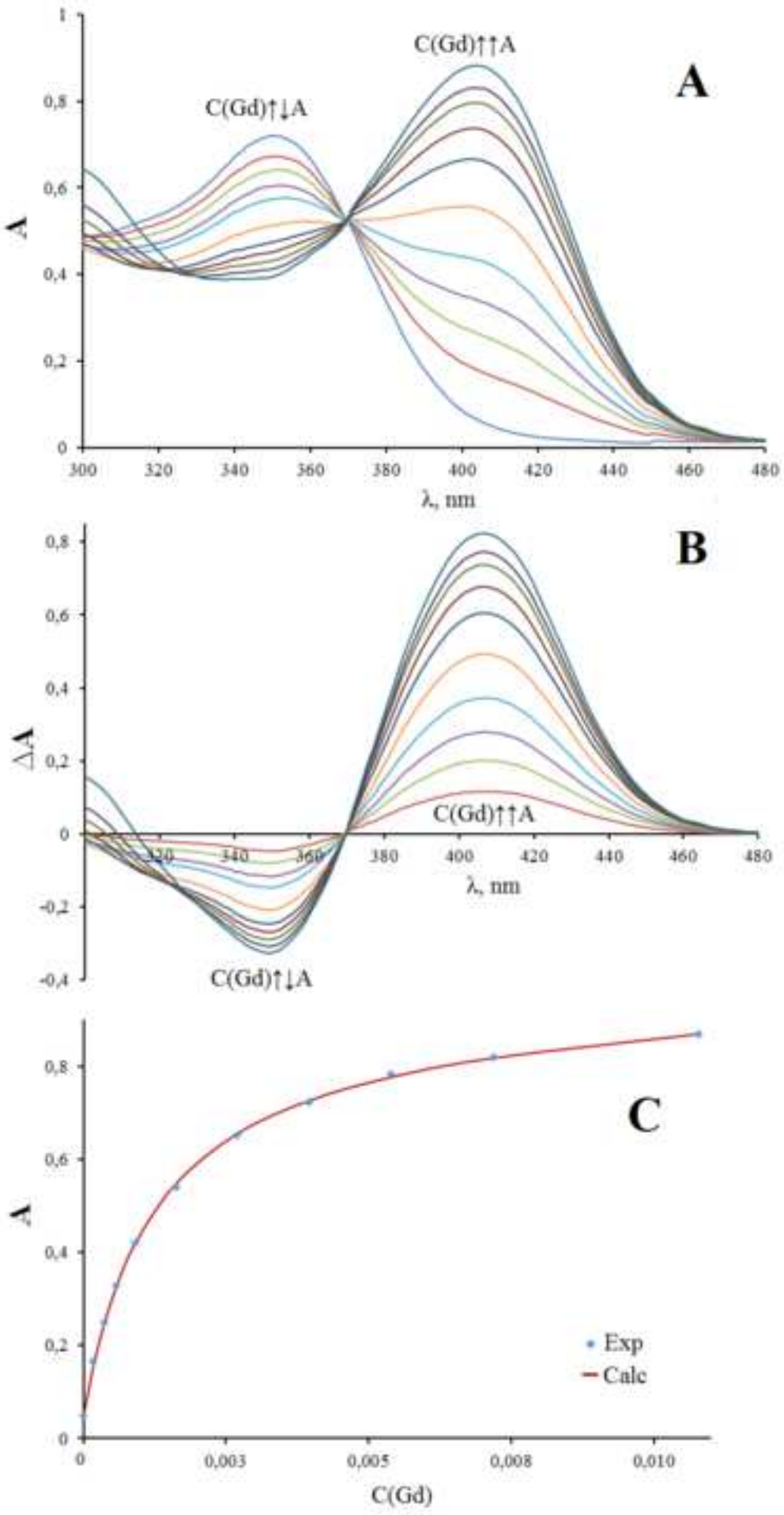

Figure 2

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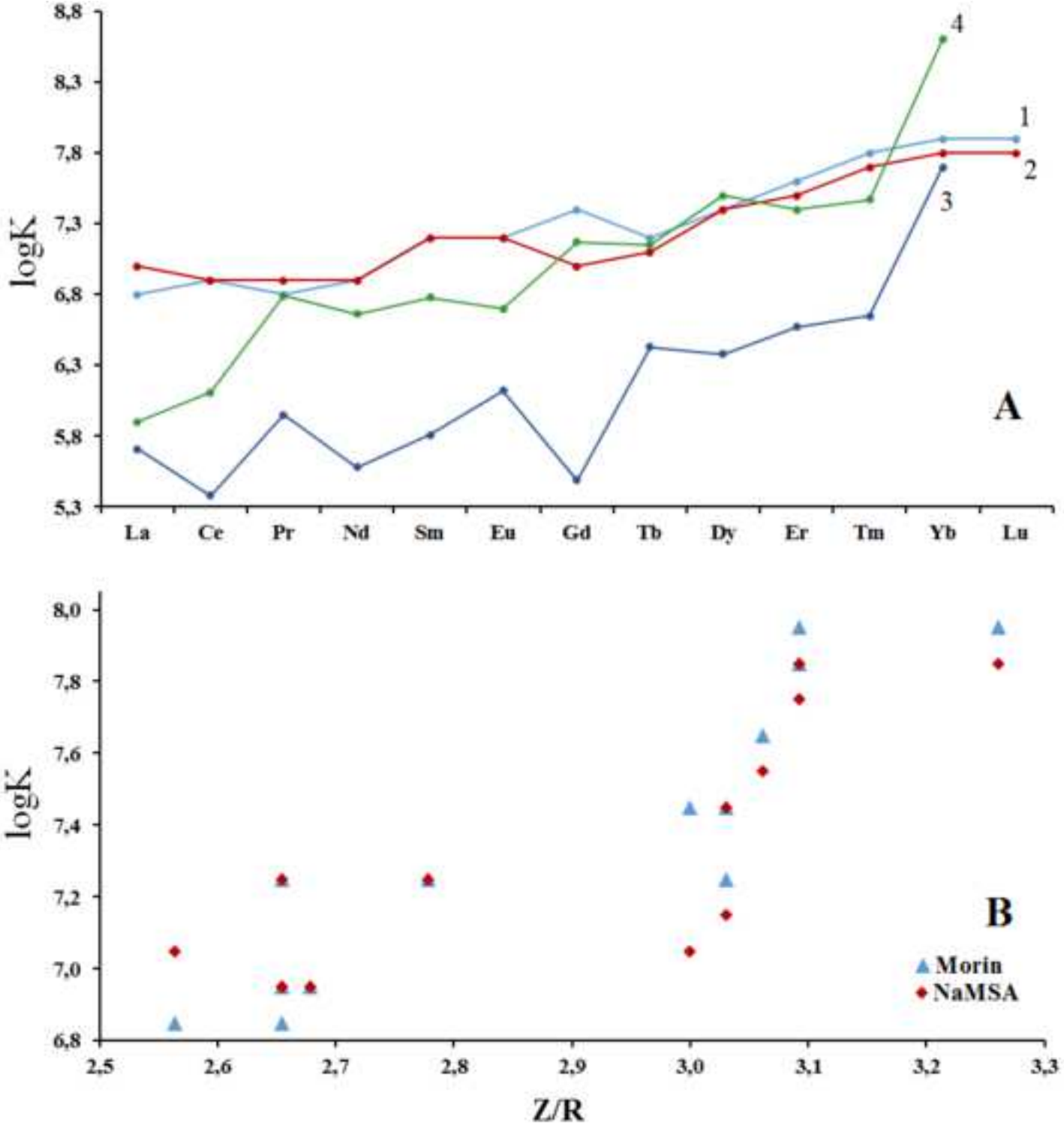

Figure 3

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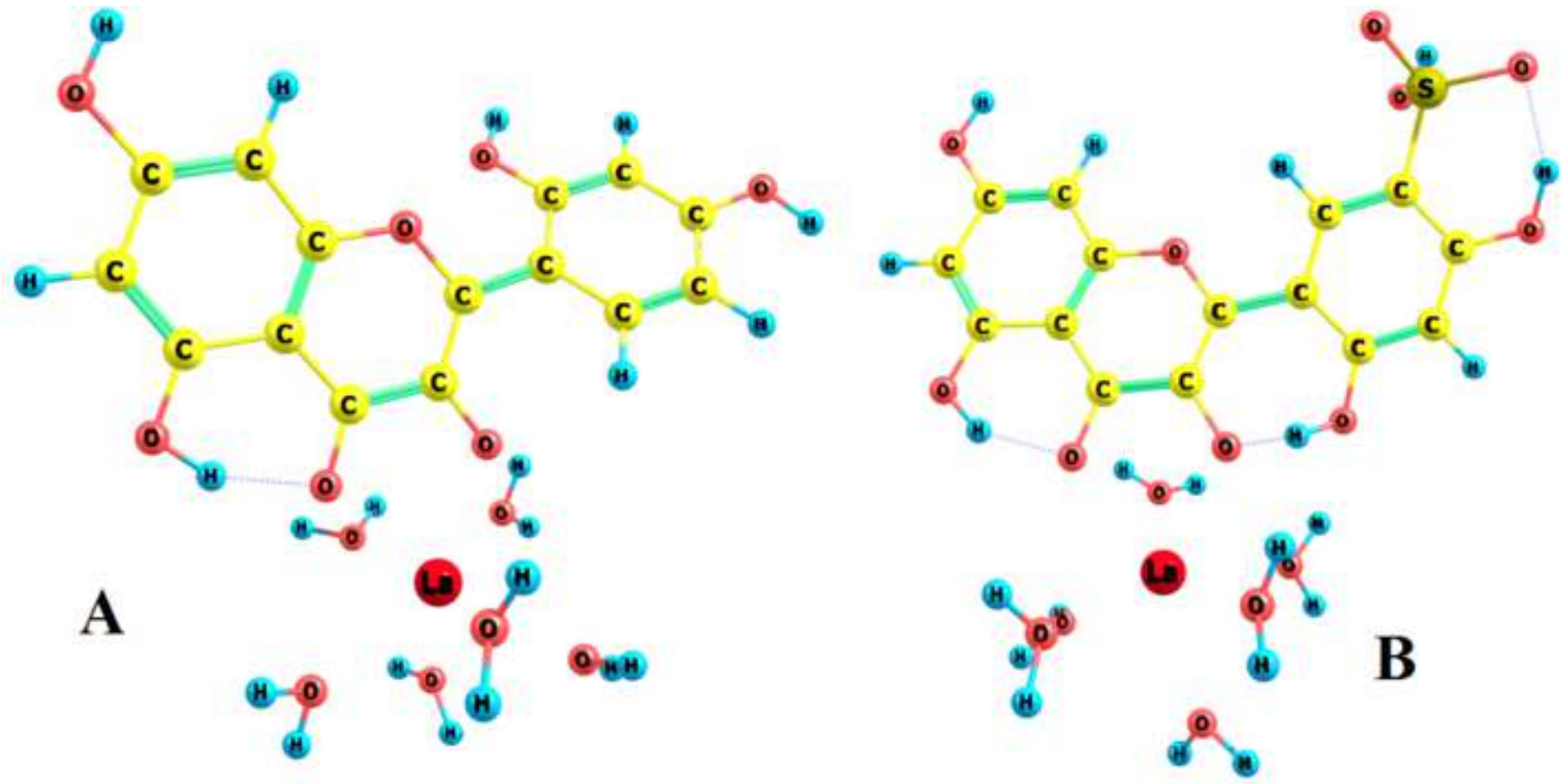

Figure 4

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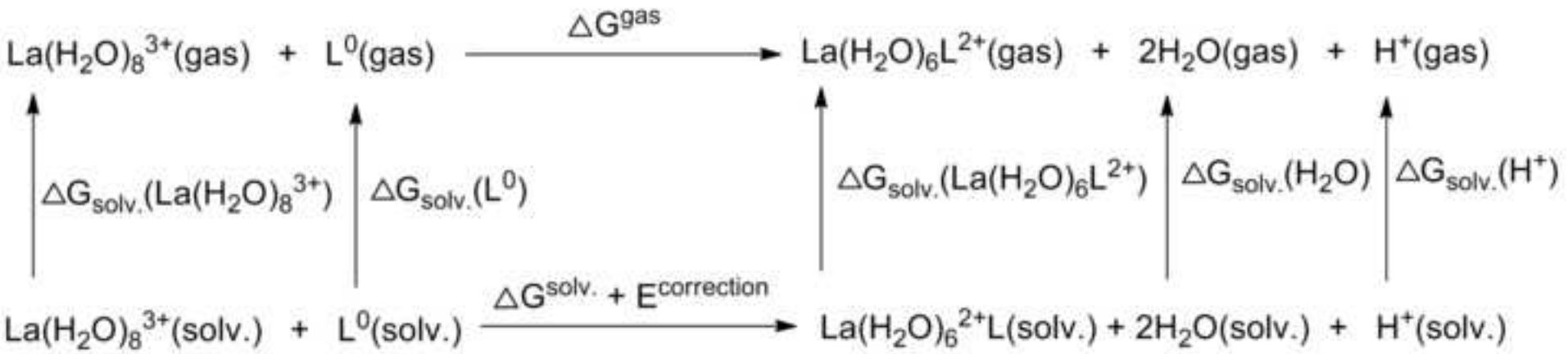

Scheme 1

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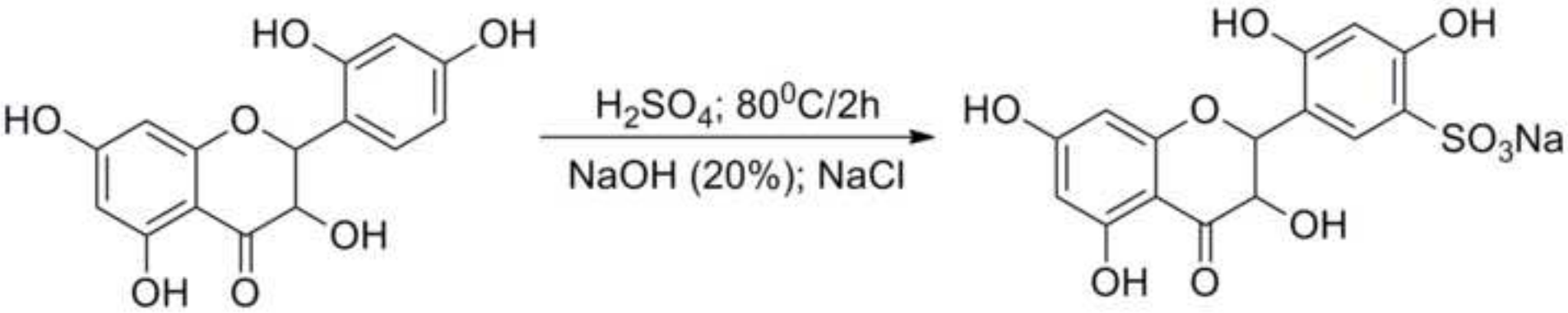

Scheme 2

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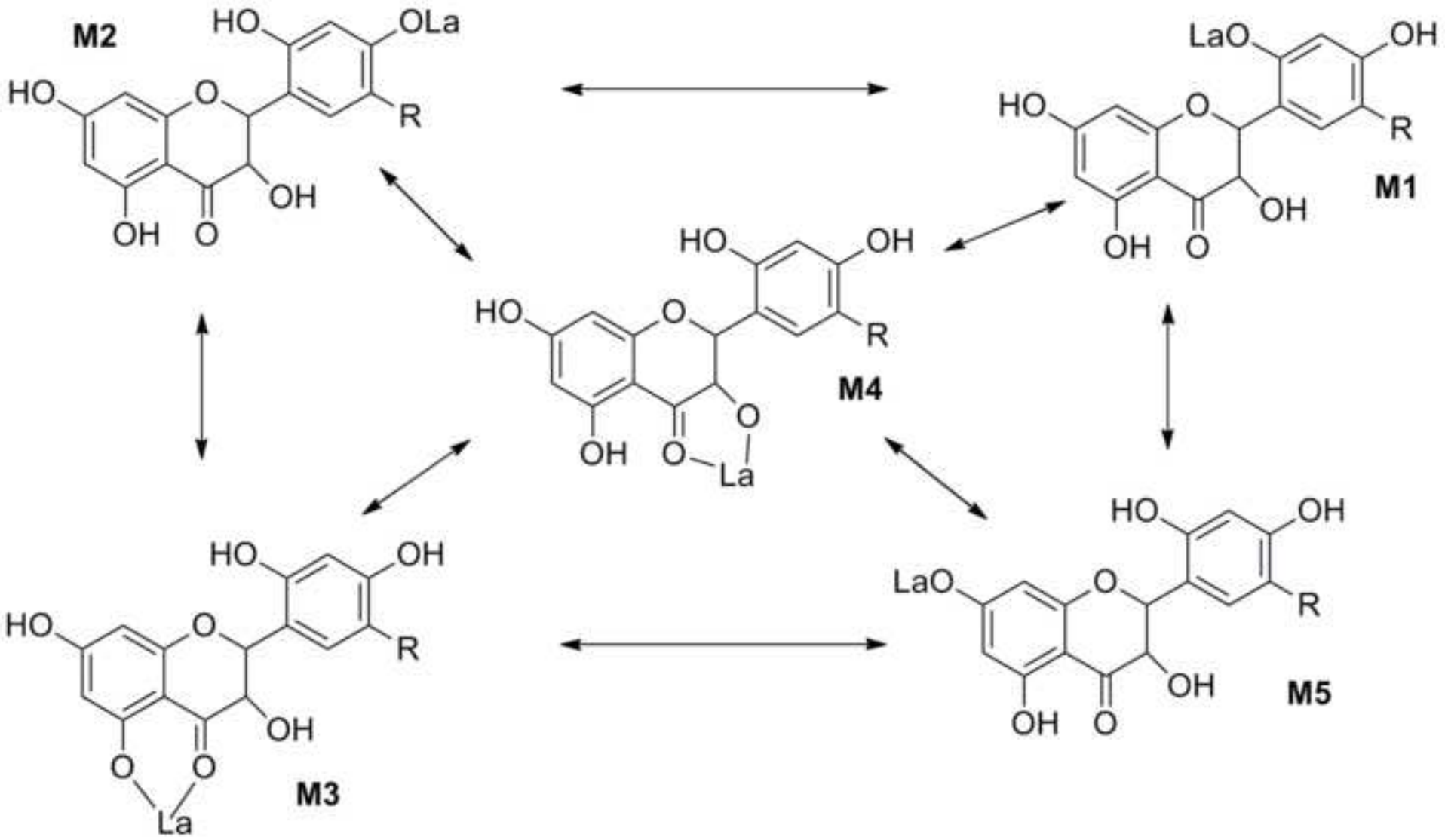

Table 1. Conditional (K'), "true" (K) stability constants and value of extinction for Morin-Ln(III) systems

Ln(III)	pH ± 0.01*	logK' ± 0.03	$\log\varepsilon^{408}$ ± 0.04	logK ± 0.1
La	2.80	2.70	4.13	6.8
Ce	2.20	1.88	4.11	6.7
	2.60	2.41	4.10	6.9
	2.80	2.64	4.15	6.9
	3.00	2.84	4.17	6.9
Pr	2.60	2.42	4.15	6.8
	2.80	2.67	4.16	6.8
	3.00	2.90	4.18	6.9
Nd	2.40	2.31	4.12	6.8
	2.60	2.54	4.13	6.9
	2.80	2.81	4.15	6.9
	3.00	3.03	4.17	7.0
Sm	2.60	2.62	4.16	7.2
Eu		2.66	4.16	7.2
Gd	2.40	2.64	4.18	7.3
	2.60	2.92	4.19	7.4
	2.80	3.17	4.19	7.4
	3.00	3.43	4.20	7.5
Tb	2.20	2.15	4.16	7.2
Dy	2.20	2.20	4.14	7.3
	2.60	2.75	4.18	7.4
	2.80	3.00	4.20	7.5
	3.00	3.25	4.20	7.5
Er	2.80	3.07	4.21	7.6
Tm		3.15	4.20	7.8**
Yb		3.17	4.21	7.9
Lu	2.40	2.70	4.05	7.9

*The "±" values represent confidence limits (P = 0.95) throughout the article.
** Estimate

Table 2. Conditional (K'), "true" (K) stability constants and value of extinction for MSA-Ln(III) systems

Ln(III)	pH ± 0.01	logK' ± 0.04	$\log\varepsilon^{408}$ ± 0.03	logK ± 0.1
La	3.00	3.62	3.79	7.0
Ce	2.80	3.21	3.88	6.9
Pr	2.40	2.81	3.77	6.8
	2.60	3.11	3.77	6.9
	2.80	3.27	3.81	6.9
	3.00	3.54	3.82	7.0
Nd	2.40	2.90	3.90	6.9
	2.60	3.08	3.88	6.8
	2.80	3.32	3.91	6.9
	3.00	3.56	3.92	6.9
Sm	2.80	3.41	3.90	7.2
Eu		3.41	3.89	7.2
Gd		3.34	3.76	7.0
Tb	2.40	2.84	3.75	7.1
Dy	2.80	3.46	3.76	7.4
Er	2.40	3.04	3.75	7.4
	2.60	3.30	3.76	7.5
	2.80	3.53	3.77	7.5
Tm	2.80	3.59	3.77	7.7*
Yb	2.40	3.09	3.76	7.7
	2.60	3.36	3.77	7.8
	2.80	3.59	3.79	7.8
Lu	2.40	3.24	3.73	7.8

* Estimate

Table 3. The calculated absolute (a.u.) and relative ($kJ \cdot mol^{-1}$) energies for La(III)-morin/MSA tautomers

tautomer	Morin (R=H)		Morinsulfanate (R=HSO_3)	
	Absolute energy	Relative energy	Absolute energy	Relative energy
M1	-1590.999137	53.6	-2214.180241	30.8
M2	-1590.989970	77.7	-2214.183390	22.5
			-2214.177208	38.7
M3	-1591.013401	16.2	-2214.180289	30.6
M4	-1591.019556	0	-2214.191964	0
M5	-1590.995547	63.0	-2214.159801	84.4

Table 4. The theoretical calculated constants and ΔG of solvation

Ligand	$logK^{exp}$	$logK^{calc}$			$-\Delta G^{solv}$, $kJ \cdot mol^{-1}$		
		Def2-SVP	Def2-TZVPD	Def2-TZVP	Def2-SVP	Def2-TZVPD	Def2-TZVP
Morin	6.80	2.09	11.88	10.55	287.53	253.39	262.40
Quercetin	5.77	1.01	8.64	7.37	262.78	253.28	253.39
MSA	7.00	4.61	10.79	9.45	283.78	273.86	282.93
QSA	5.90	3.40	9.57	8.31	239.75	230.32	240.05

K. Iftikhar; Department of Chemistry , Lanthanide Research Laboratory , Jamia Millia Islamia, New Delhi-110 025 , India, : kiftikhar@jmi.ac.in

Mariola Samsonowicz; Bialystok University of Technology, Division of Chemistry, Wiejska 45E, 15-351 Bialystok, Poland: samsonowicz@pb.edu.pl

Anamaria D. P. Alexiou; a Escola de Engenharia, Universidade Presbiteriana Mackenzie, São Paulo, Brazil; anamaria.alexiou@mackenzie.br

R. Ravichandran; Department of Chemistry, Centre for Research and Post Graduate Studies in Chemistry, N. M. S. S. Vellaichamy Nadar College, Madurai, India: mrrajendran64@yahoo.com

The Aqueous Complexation of Morin and its Sulfonate Derivative with Lanthanum(III) and Trivalent Lanthanide

Supplementary materials

Maxim A. Lutoshkin[a,b§], Alexander I. Petrov[b], Boris N. Kuznetsov[b,c] and Alexandr S. Kazachenko[b]

[a]Université de Lyon, Université Claude Bernard Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, France

[b]Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS", Krasnoyarsk, Russian Federation

[c]Institute of Non-Ferrous Metals and Materials Science, Siberian Federal University, Krasnoyarsk, Russian Federation

*Corresponding author e-mail: maximsfu@yahoo.com

Table S1. The absorbance data for Ce-Morin system for 408 nm

C(Morin) = $6.64\cdot10^{-5}$ M				C(Morin) =$5.85\cdot10^{-5}$ M		C(Morin) = $6.64\cdot10^{-5}$ M	
pH 2.20		pH 2.60		pH 2.80		pH 3.00	
C(Ce), M	A	C(Ce), M	A	C(Ce), M	A	C(Ce), M	A
0	0.048	0	0.059	0	0.050	0	0.056
0.002	0.149	0.001	0.221	0.0004	0.170	0.0004	0.267
0.004	0.206	0.002	0.326	0.0008	0.256	0.0010	0.433
0.006	0.272	0.003	0.408	0.0016	0.371	0.0018	0.562
0.008	0.32	0.004	0.464	0.0028	0.491	0.0028	0.649
0.012	0.398	0.005	0.505	0.0044	0.566	0.0040	0.726
0.016	0.451	0.006	0.550	0.0064	0.638	0.0060	0.793
0.020	0.491	0.005	0.612	0.0088	0.698	0.0090	0.851
0.030	0.564	0.012	0.698	0.0120	0.754	0.0140	0.912
0.040	0.625	0.016	0.742	0.0160	0.786	0.2000	0.942
		0.020	0.773				

Table S2. The absorbance data for Pr-Morin system for 408 nm, C(Morin) = $5.95 \cdot 10^{-5}$ M

pH 2.60		pH 2.80		pH 3.00	
C(Pr), M	A	C(Pr), M	A	C(Pr), M	A
0.0004	0.119	0.0004	0.170	0.0004	0.240
0.0009	0.207	0.0009	0.302	0.0070	0.359
0.0016	0.291	0.0016	0.402	0.0013	0.480
0.0027	0.382	0.0025	0.498	0.0022	0.585
0.0040	0.459	0.0040	0.577	0.0036	0.676
0.0058	0.527	0.0054	0.643	0.0054	0.735
0.0080	0.592	0.0080	0.696	0.0080	0.790
0.0109	0.654	0.0109	0.751	0.0011	0.831
0.0145	0.698	0.0145	0.784	0.0145	0.848

Table S3. The absorbance data for Nd-Morin system for 408 nm

C(Morin) = $6.87 \cdot 10^{-5}$ M		C(Morin)=$5.95 \cdot 10^{-5}$ M					
pH 2.40		pH 2.60		pH 2.80		pH 3.00	
C(Nd), M	A	C(Nd), M	A	C(Nd), M	A	C(Nd), M	A
0.0006	0.144	0.0004	0.135	0.0002	0.157	0.0003	0.265
0.0013	0.239	0.0010	0.240	0.0006	0.259	0.0006	0.375
0.0023	0.327	0.0017	0.333	0.0011	0.394	0.0011	0.489
0.0034	0.412	0.0029	0.433	0.0019	0.485	0.0017	0.581
0.0050	0.490	0.0042	0.508	0.0029	0.566	0.0027	0.660
0.0069	0.565	0.0061	0.581	0.0042	0.641	0.0042	0.731
0.0096	0.642	0.0084	0.637	0.0061	0.697	0.0061	0.787
0.0122	0.690	0.0115	0.691	0.0084	0.752	0.0084	0.820
0.0153	0.734	0.0153	0.732	0.0115	0.790	0.0115	0.846
				0.0153	0.822		

Table S4. The absorbance data for Sm-Morin and Eu-Morin systems for 408 nm, pH = 2.60

C(Morein) = $5.85 \cdot 10^{-5}$ M		C(Morein) = $6.64 \cdot 10^{-5}$ M	
C(Sm), M	A	C(Eu), M	A
0.001	0.330	0.001	0.295
0.002	0.467	0.002	0.415
0.003	0.560	0.003	0.507
0.004	0.624	0.004	0.578
0.006	0.705	0.006	0.643
0.008	0.767	0.008	0.692
0.012	0.839	0.012	0.769
0.020	0.904	0.018	0.790
		0.020	0.813

Table S5. The absorbance data for Gd-Morin system for 408 nm

C(Morin)=$5.95 \cdot 10^{-5}$ M		C(Morin)=$5.85 \cdot 10^{-5}$ M		C(Morin)=$5.95 \cdot 10^{-5}$ M			
pH 2.40		pH 2.60		pH 2.80		pH 3.00	
C(Gd), M	A	C(Gd), M	A	C(Gd), M	A	C(Gd), M	A
0.0005	0.201	0.0002	0.165	0.0002	0.228	0.0001	0.234
0.0011	0.326	0.0004	0.249	0.0004	0.343	0.0002	0.340
0.0018	0.427	0.0007	0.327	0.0006	0.455	0.0004	0.475
0.0027	0.517	0.0011	0.421	0.0010	0.572	0.0006	0.587
0.0040	0.595	0.0020	0.541	0.0016	0.668	0.0010	0.689
0.0058	0.675	0.0033	0.653	0.0025	0.752	0.0016	0.765
0.0079	0.731	0.0048	0.724	0.0040	0.817	0.0025	0.831
0.0108	0.781	0.0066	0.785	0.0072	0.851	0.0041	0.889
		0.0087	0.820			0.0054	0.908
		0.0131	0.870				

Table S6. The absorbance data for Dy-Morin system for 408 nm

C(Morin) = $8.35 \cdot 10^{-5}$ M				C(Morin) = $5.85 \cdot 10^{-5}$ M			
pH 2.20		pH 2.60		pH 2.80		pH 3.00	
C(Dy), M	A	C(Dy), M	A	C(Dy), M	A	C(Dy), M	A
0.001	0.216	0.0002	0.185	0.0002	0.202	0.0002	0.286
0.002	0.335	0.0004	0.288	0.0004	0.291	0.0004	0.407
0.003	0.426	0.0006	0.356	0.0006	0.375	0.0006	0.490
0.004	0.497	0.0010	0.501	0.0010	0.478	0.0008	0.546
0.006	0.606	0.0018	0.661	0.0018	0.608	0.0012	0.641
0.009	0.720	0.0030	0.806	0.0030	0.709	0.0020	0.732
0.012	0.826	0.0045	0.933	0.0045	0.779	0.0030	0.796
0.016	0.898	0.0061	1.005	0.0061	0.818	0.0045	0.841
0.200	0.956	0.0081	1.078	0.0098	0.880	0.0061	0.879
		0.0142	1.182	0.0137	0.904	0.0081	0.898
		0.0203	1.251			0.0101	0.923

Table S7. The absorbance data for Tb, Yb, Tm, Er-Morin systems for 408 nm;
C(Morin) = $5.85 \cdot 10^{-5}$ M

pH 2.20		pH 2.80					
C(Tb), M	A	C(Yb), M	A	C(Tm), M	A	C(Er), M	A
0.002	0.238	0.0002	0.268	0.0001	0.201	0.0002	0.196
0.004	0.354	0.0004	0.383	0.0003	0.316	0.0003	0.295
0.007	0.428	0.0007	0.488	0.0005	0.408	0.0005	0.382
0.010	0.505	0.0010	0.580	0.0008	0.506	0.0008	0.486
0.014	0.587	0.0017	0.679	0.0013	0.616	0.0015	0.615
0.020	0.639	0.0027	0.772	0.0020	0.706	0.0024	0.711
0.027	0.700	0.0041	0.834	0.0030	0.774	0.0036	0.785
0.036	0.746	0.0062	0.885	0.0044	0.836	0.0049	0.828
		0.0083	0.913	0.0060	0.871	0.0065	0.865

Table S8. The absorbance data for La, Lu-Morin systems for 408 nm; C(Morin) = $5.95 \cdot 10^{-5}$ M

pH 2.40		pH 2.80	
C(Lu), M	A	C(La), M	A
0.0004	0.165	0.0003	0.140
0.0008	0.239	0.0006	0.210
0.0013	0.301	0.0008	0.269
0.0021	0.375	0.0012	0.331
0.0031	0.439	0.0017	0.391
0.0047	0.507	0.0022	0.441
0.0063	0.551	0.0034	0.527
0.0083	0.602	0.0045	0.576
0.0104	0.637		

Table S9. The absorbance data for La, Ce-NaMSA systems for 408 nm

C(NaMSA) = $1.11 \cdot 10^{-4}$		C(NaMSA) = $1.03 \cdot 10^{-4}$	
pH 3.00		pH 2.80	
C(La), M	A	C(Ce), M	A
0.0001	0.257	0.0002	0,244
0.0003	0.373	0.0004	0,326
0.0006	0.487	0.0010	0,484
0.0010	0.554	0.0019	0,594
0.0015	0.596	0.0033	0,669
0.0022	0.637	0.0052	0,713
0.0034	0.651	0.0080	0,751
		0.0120	0.781

Table S10. The absorbance data for Pr-NaMSA systems for 408 nm; C(NaMSA) = $1.11 \cdot 10^{-4}$ M

pH 2.40		pH 2.60		pH 2.80		pH 3.00	
C(Pr), M	A	C(Pr), M	A	C(Pr), M	A	C(Pr), M	A
0.0004	0.183	0.0002	0.190	0.0002	0.241	0.0002	0.327
0.0007	0.240	0.0004	0.253	0.0004	0.313	0.0004	0.420
0.0011	0.311	0.0007	0.334	0.0006	0.413	0.0007	0.517
0.0019	0.390	0.0011	0.409	0.0011	0.502	0.0011	0.589
0.0031	0.449	0.0019	0.481	0.0019	0.572	0.0019	0.647
0.0050	0.515	0.0031	0.543	0.0031	0.628	0.0031	0.684
0.0076	0.570	0.0050	0.603	0.0050	0.667	0.0050	0.713

Table S11. The absorbance data for Nd-NaMSA systems for 408 nm

C(NaMSA) = $8.18 \cdot 10^{-5}$ M		C(NaMSA) = $1.11 \cdot 10^{-4}$ M					
pH 2.40		pH 2.60		pH 2.80		pH 3.00	
C(Nd), M	A	C(Nd), M	A	C(Nd), M	A	C(Nd), M	A
0.0004	0.200	0.0004	0.287	0.0002	0.301	0.0002	0.341
0.0007	0.261	0.0010	0.444	0.0006	0.463	0.0003	0.452
0.0011	0.334	0.0017	0.535	0.0011	0.583	0.0005	0.566
0.0019	0.411	0.0029	0.631	0.0018	0.672	0.0010	0.659
0.0031	0.476	0.0042	0.672	0.0029	0.719	0.0017	0.742
0.0050	0.542	0.0061	0.721	0.0042	0.763	0.0027	0.784
0.0076	0.587	0.0084	0.747	0.0061	0.793	0.0042	0.813
		0.0115	0.784	0.0096	0.815	0.0061	0.831

Table S12. The absorbance data for Eu-,Sm-,Gd-NaMSA systems for 408 nm; pH=2.80

C(NaMSA) = $1.03 \cdot 10^{-4}$ M				C(NaMSA) = $1.07 \cdot 10^{-4}$ M	
C(Sm), M	A	C(Eu), M	A	C(Gd), M	A
0.0003	0.359	0.0003	0.358	0.0002	0.217
0.0006	0.511	0.0006	0.493	0.0004	0.292
0.0011	0.615	0.0011	0.610	0.0006	0.371
0.0020	0.699	0.0020	0.694	0.0010	0.436
0.0034	0.757	0.0034	0.731	0.0016	0.492
0.0052	0.794	0.0052	0.782	0.0025	0.536
0.0080	0.821	0.0080	0.811	0.0040	0.569

Table S13. The absorbance data for Tb-,Dy-NaMSA systems for 408 nm
C(NaMSA) = $1.07 \cdot 10^{-4}$ M

pH 2.40		pH 2.80	
C(Tb), M	A	C(Dy), M	A
0.0009	0.269	0.0002	0.255
0.0015	0.338	0.0004	0.345
0.0025	0.406	0.0007	0.415
0.0040	0.459	0.0011	0.481
0.0062	0.503	0.0018	0.532
0.0098	0.543	0.0027	0.568
0.0142	0.565	0.0043	0.594

Table S14. The absorbance data for Er-NaMSA systems for 408 nm

C(NaMSA) = $1.26 \cdot 10^{-4}$ M				C(NaMSA) = $1.07 \cdot 10^{-4}$ M	
pH 2.40		pH 2.60		pH 2.80	
C(Er), M	A	C(Er), M	A	C(Er), M	A
0.0003	0.237	0.0003	0.314	0.0002	0.254
0.0058	0.310	0.0059	0.411	0.0003	0.343
0.0010	0.384	0.0010	0.492	0.0006	0.417
0.0016	0.475	0.0016	0.569	0.0010	0.492
0.0026	0.550	0.0026	0.628	0.0016	0.548
0.0039	0.602	0.0039	0.671	0.0026	0.582
0.0052	0.633	0.0052	0.697	0.0039	0.608

Table S15. The absorbance data for Yb-NaMSA systems for 408 nm

C(NaMSA) = $1.00 \cdot 10^{-4}$ M		C(NaMSA) = $1.26 \cdot 10^{-4}$ M			
pH 2.40		pH 2.60		pH 2.80	
C(Yb), M	A	C(Yb), M	A	C(Yb), M	A
0.0004	0.235	0.0002	0.277	0.0004	0.483
0.0007	0.311	0.0004	0.375	0.0007	0.573
0.0012	0.380	0.0007	0.460	0.0012	0.645
0.0021	0.451	0.0012	0.555	0.0021	0.697
0.0033	0.504	0.0021	0.622	0.0033	0.728
0.0050	0.542	0.0033	0.670	0.0050	0.746
0.0066	0.570	0.0050	0.698	0.0066	0.761

Table S16. The absorbance data for Tm-, Lu-NaMSA systems for 408 nm

C(NaMSA) = $1.07 \cdot 10^{-4}$ M		C(NaMSA) = $1.11 \cdot 10^{-4}$ M	
pH 2.80		pH 2.40	
C(Tm), M	A	C(Lu), M	A
0.0001	0.213	0.0003	0.232
0.0002	0.289	0.0005	0.308
0.0003	0.363	0.0009	0.383
0.0060	0.448	0.0016	0.464
0.0010	0.505	0.0026	0.520
0.0016	0.552	0.0042	0.573
0.0032	0.603	0.0063	0.609

I=1.

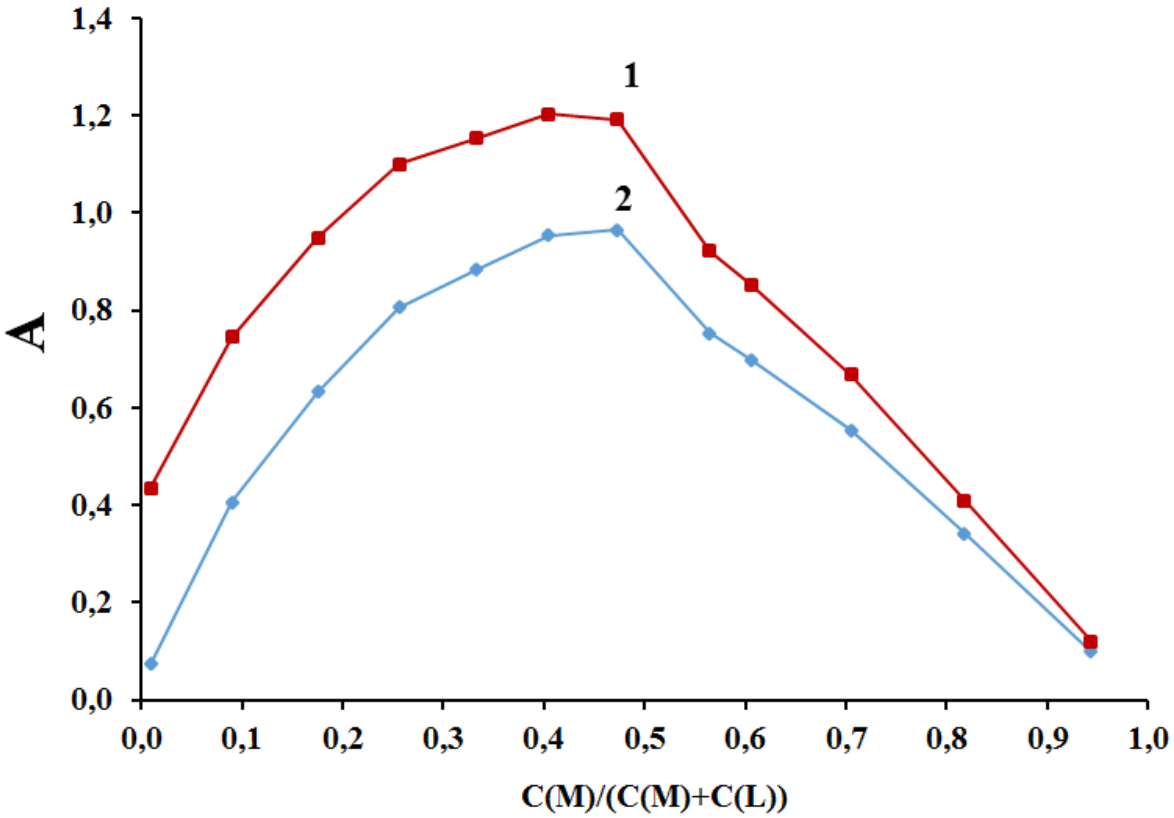

Figure S1. The Job method for Gd(III)-Morin system. Curve 1 –absolute absorbance; Curve 2 - ΔA; pH=3.00; I=1.

Table S17. The logK values for calculation of α_m and α_L

Ln(III)	Gycine-Ln(III)	OH-Ln(III)
La	3.2	9.12
Ce	3.4	8.65
Pr	3.3	8.62
Nd	3.3	8.49
Sm	3.5	8.15
Eu	3.5	8.06
Gd	3.4	8.14
Tb	3.6	7.95
Dy	3.6	7.89
Er	3.7	7.82
Tm	3.8*	7.00
Yb	3.9	7.55
Lu	3.9	6.24

*Estimate